Liquid Crystals

1,4-Diaryl and Schiff's base [1,2,3]-triazole derivative liquid crystalline compounds

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Regioselective synthesis of [1,2,3]-triazoles based on the 'click-reaction', involving the Cu(I)-catalysed 1,3-dipolar cycloaddition of aryl azide to terminal arylacetylenes, was successfully employed in the preparation of two series of non-linear mesogens, based on 1,4-diaryl-[1,2,3]-triazole (**Ia–e**) and with Schiff's base units (**IIa–c**). Their mesophases were characterized by polarizing optical microscopy and differential scanning calorimetry. All final compounds exhibited preferentially the SmC phase. In addition, compounds of series **I** showed weak blue fluorescence in solution ($\lambda_{\text{max. em.}} = 380$–386 nm) with poor quantum yields and a Stokes shift of around 90 nm.

1. Introduction

Liquid crystals containing heterocyclic units are of crucial importance in the design and synthesis of novel advanced functional materials, where liquid crystalline phases, polarity, geometry, luminescence and others properties of the molecule may be varied through the introduction of heteroatoms [1, 2]. Furthermore, luminescent liquid crystals are of interest since their self-organizing properties can be exploited to improve device performance and to achieve linearly polarized electroluminescence [3]. [1,2,3]-Triazole comprises an unnatural *N*-heterocyclic ring which gives this molecule a high level of biological activity [4], and also a great potential in materials chemistry for the production of dyes, corrosion inhibitors, photostabilizers and photographic materials [5]. Some [1,2,3]-triazole derivative compounds exhibit fluorescence [6], as studied by Wang *et al.* in relation to their bioconjugation and bioimaging applications [7].

The most useful technique available to prepare this five-membered ring heterocycle is the 1,3-dipolar cycloaddition of azides to alkynes (Huisgen reaction), which is known as the 'cream of the crop' of click chemistry reactions [8]. Combinations of the substituents on alkyne and azide allow the synthesis of many *N*-substituted structures. The employment of a catalytic amount of Cu(I) or Cu(II) salts and sodium ascorbate, with water as the solvent, plays an important role in the control of the 1,4-regioselectivity [9, 10]. The catalytic

mechanism has been investigated in detail by Fahmi *et al.*, who recently proposed a consistent cycle [11]. The click-reaction has been applied successfully by our group in the synthesis of new [1,2,3]-triazole derivative chiral mesogens which showed SmA, SmC* and helical N* (cholesteric) phases [10, 12]. Also, we have previously described the synthetic procedure for regioselective synthesis of 1,4-diaryl-[1,2,3]-triazole with a non-linear shape (compounds **Ia–e**, figure 1) [13].

In this paper, we report the mesomorphic behaviour and photophysical properties for compounds **Ia–e** and the synthesis of a further three new [1,2,3]-triazole-based mesogens containing Schiff's base units (compounds **IIa–c**, figure 1), by applying the click-reaction, as well as their mesomorphic behaviour. The triazole unit plays an important role since it acts as a linker between the conjugated segments of the compound and also because it has a good electron affinity, potentially acting as an electron-transporting material.

2. Results and discussion

2.1. *Synthesis*

The final compounds **Ia–e** were prepared with a high degree of purity and in good chemical yields through the Cu(I)-catalysed 'click-reaction' between 1-azido-4-decyloxybenzene **2** and the respective terminal arylacetylenes, using a mixture of ethanol/water and catalytic amounts of Cu(I) and triethylamine (TEA) as the additive [13] (scheme 1). Under the same conditions it was possible to prepare the [1,2,3]-triazole ring from

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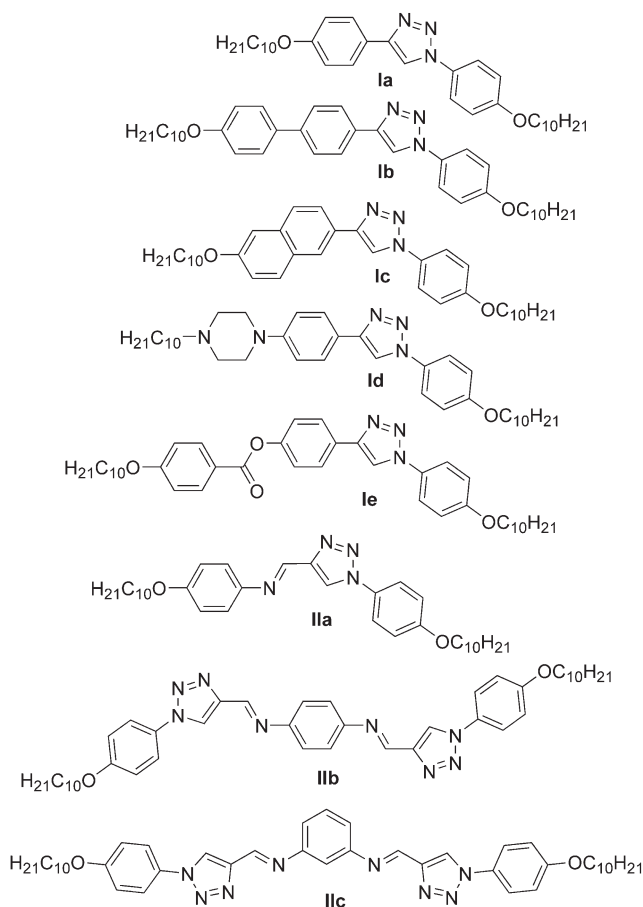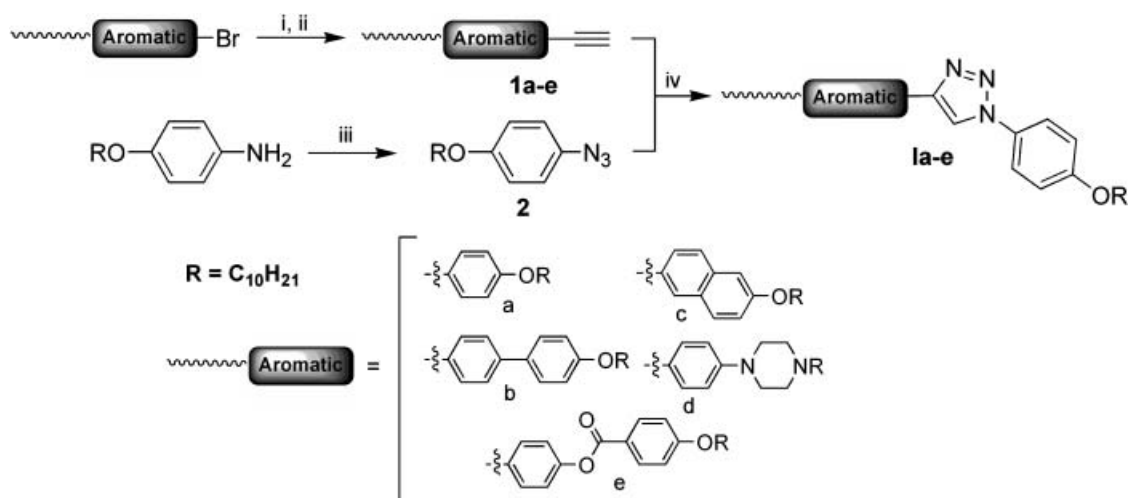*Corresponding author. Email: hugo@qmc.ufsc.br

Figure 1. Chemical structures of the final synthesized molecules.

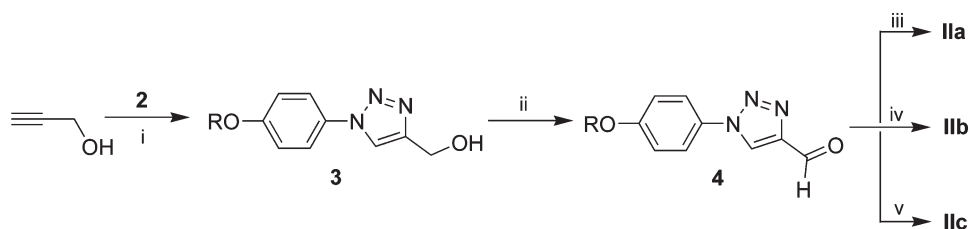propargyl alcohol and compound **2**, furnishing compound **3** (scheme 2). The alcohol was oxidized by manganese (II) oxide to give compound **4**, a building block containing the aldehyde unit, which was further reacted with the respective arylamines affording final compounds **IIa–c** with Schiff's base units.

2.2. Mesophases and thermal properties

All the compounds showed liquid crystalline behaviour, in particular the smectic C phase (SmC) which appeared to be dominant in all the structures (figure 2). The transition temperatures and phase assignments for the materials were investigated by thermal polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The optical observations were performed using clean untreated glass slides. The results are given in table 1.

In a previous study we reported that displacement of the heterocycle [1,2,3]-triazole to the central position in a chiral liquid crystal resulted in it showing the SmA* phase, and lowered the melting point significantly in comparison with compounds containing the [1,2,3]-triazole in the terminal position [12]. However, the thermal results for compounds **Ia–e** indicate that elongation of the aromatic core stabilizes the SmC phase and the SmA phase disappears completely. Compound **Ia**, with only three aromatic rings, exhibits the shortest LC range with SmA and SmC phases. Although DSC analysis could not be used effectively to separate the SmC–SmA from SmA–I transitions, the presence of the SmA phase was confirmed through microscopy. This phase separates out from the dark isotropic liquid in the form of bâtonnets which coalesce and build up the characteristic focal-conic texture, figure 3(*a*). On cooling, the focal-conics develop into the broken fan-shaped texture typical of the SmC phase, figure 3(*b*).

Scheme 1. Reagents: i. 2-Methyl-3-butyn-2-ol, PdCl$_2$(PPh$_3$)$_2$, CuI, TPP, TEA; ii. NaOH, toluene; iii. 1) NaNO$_2$, HCl, H$_2$O; 2) NaN$_3$; iv. CuI, TEA, H$_2$O/EtOH 1/1.

Scheme 2. Reagents: i. **2**, CuI, TEA, H_2O/EtOH 1/1; ii. MnO_2, CH_2Cl_2; iii. 4-decyloxyaniline, EtOH; iv. *p*-phenylenediamine, EtOH; v. *m*-phenylenediamine dihydrochloride, EtOH.
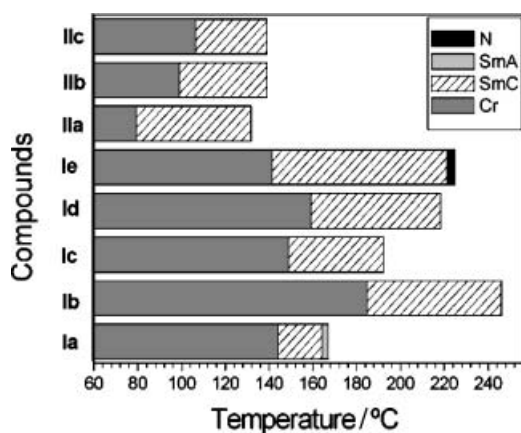
Figure 2. Comparative mesomorphic profile of the final compounds.

Table 1. Transition temperatures (°C) and enthalpy changies (ΔH/kJ mol^{-1}), in parenthese of final compounds **Ia**–**e** and **IIa**–**c**: determined by optical microscopy and DSC measurements 10°C min^{-1}.

Compound	Transition	Heating	Cooling
Ia	CrI–CrII	138.2 (21.6)	114.5 (−27.8)
	CrII–SmC	144.2 (20.2)	140.0 (−23.4)
	SmC–SmA	164.1 (broad)	160.8 (broad)
	SmA–I	167.2 (8.90)	166.3 (−9.16)
Ib	CrI–CrII	136.3 (2.70)	130.6 (−2.90)
	CrII–SmC	184.9 (30.3)	178.1 (−26.0)
	SmC–I	246.1 (6.98)	242.3 (−6.83)
Ic	Cr–SmC	148.8 (37.3)	129.0 (−37.0)
	SmC–I	192.4 (7.77)	191.3 (−7.96)
Id	Cr–SmC	159.4 (12.7)	153.5 (−12.8)
	SmC–I	218.3 (7.29)	212.3 (−5.60)
Ie	Cr–SmC	141.6 (24.8)	131.8 (−19.1)
	SmC–N	221.5 (3.16)	220.1 (−3.62)
	N–I	224.8 (1.11)	223.5 (−1.65)
IIa	Cr–SmC	79.58 (31.2)	76.70 (−39.7)
	SmC–I	131.7 (8.09)	128.7 (−7.59)
IIb	Cr–SmC	98.99 (19.7)	93.42 (−18.1)
	SmC–I	138.9 (broad)	136.0 (broad)
IIc	Cr–SmC	106.5 (26.6)	101.8 (−26.5)
	SmC–I	139.0 (8.58)	135.7 (−8.35)
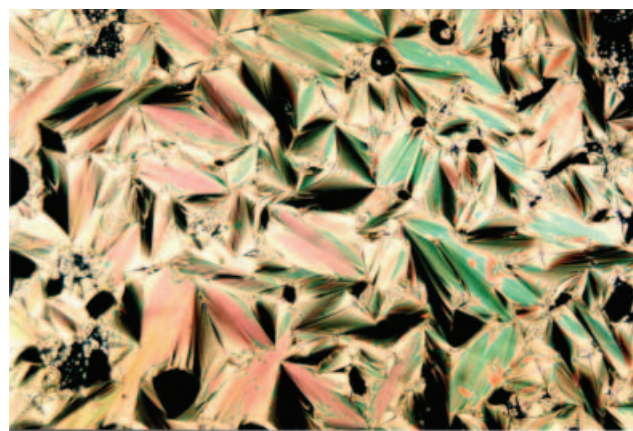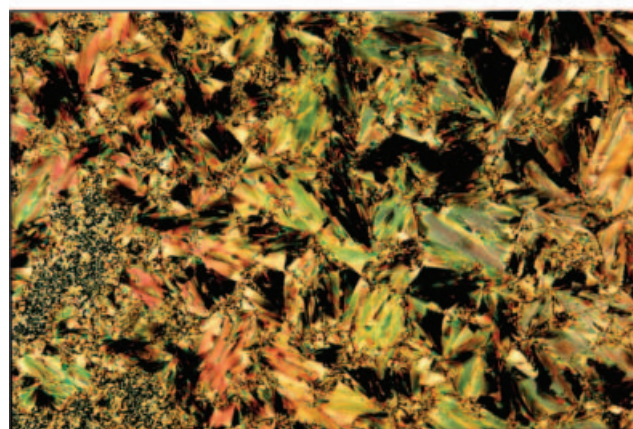
Figure 3. Photomicrographs of (*a*) the focal-conic texture of the SmA phase at 166°C and (*b*) the broken fan-shaped texture of the SmC phase at 164.1°C for compound **Ia** (33x).

Compounds **Ib**, **c** and **d** with biphenyl, naphthyl and phenylpiperazine in the aromatic rigid core, respectively, show only the SmC phase within a large temperature range. For all of them, on cooling from the isotropic liquid, bâtonnets appear which develop into a broken-fan shaped texture (figure 4).

Compound **Ie** showed the largest LC temperature range of around 80°C, with the SmC phase and a short nematic phase. The DSC thermograms for this
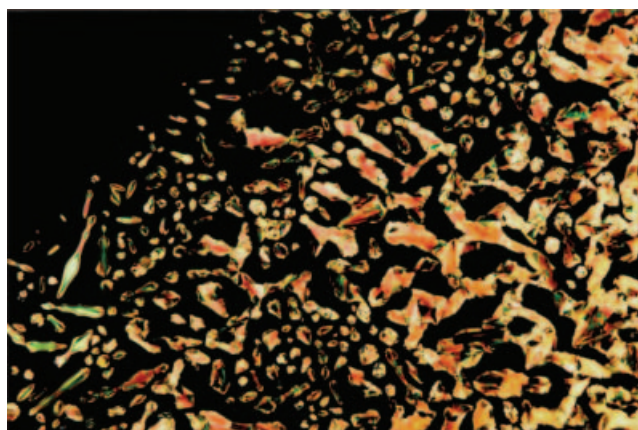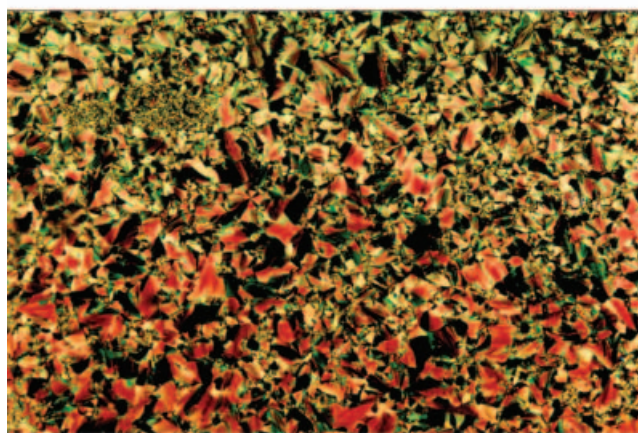
Figure 4. Representative photomicrographs for compounds showing only the SmC phase: (*a*) appearance of bâtonnets at 191.5°C on cooling the isotropic liquid entering in the SmC phase, and (*b*) further cooling leading to a broken fan-shaped SmC texture at 179.6°C for compound **Ic** (33x).

compound are shown in figure 5. On heating, the compound melts to the SmC phase at 141.6°C and goes to the nematic phase just below the clearing point at 224.8°C. At a rate of $10°C \, min^{-1}$, it was impossible to separate the two peaks in the DSC thermogram, figure 5(*a*), but with a low rate of $1°C \, min^{-1}$, in the region 210–250°C, these peaks were well defined, figure 5(*b*), and the N–I and SmC–N transitions established. The low enthalpy value of around $1 \, kJ \, mol^{-1}$ is characteristic of an N–I transition, which was also confirmed by optical microscopy. Upon cooling the schlieren nematic texture changes to the schlieren SmC phase with a clearly visible fingerprint region between the two phases, characterizing a N–SmC transition.

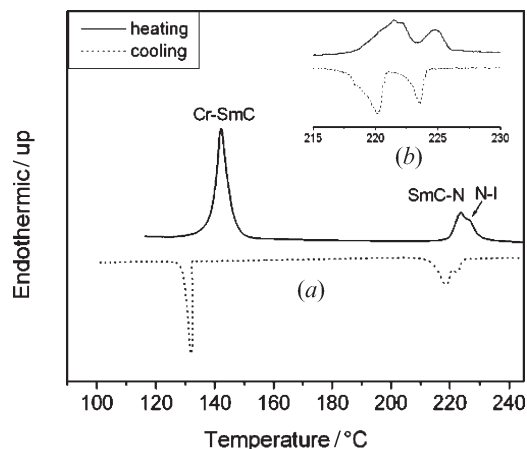Schiff's base derivatives **IIa**–**c** showed only SmC phases with a schlieren texture observed by microscopy.

Figure 5. (*a*) Thermogram obtained by DSC analysis at $10°C \, min^{-1}$ showing the thermal transitions for compound **Ie**. (*b*) Thermogram in the region from 215 to 230°C at $1°C \, min^{-1}$ showing the separation of SmC–N and N–I transition peaks for compound **Ie**.

Melting points of these compounds were lower than those of the series **Ia**–**e**, even though **IIb** and **c** possess five aromatic rings. This observation is due to the presence of an imine group. The different substitution pattern on the benzene central core (*para* and *meta*) in compounds **IIb** and **c** was not sufficient to promote significant changes in the calamitic mesomorphic behaviour, as expected. This may be due to the presence of five-membered rings in which the 1,4 substitution (not collinear) recovers the linearity lost by the 1,3-substituted benzene core in compound **IIc**. A typical thermogram obtained by DSC analysis of compound **IIc** is presented in figure 6. On heating, the compound melts at 106.5°C to the SmC phase and goes to an
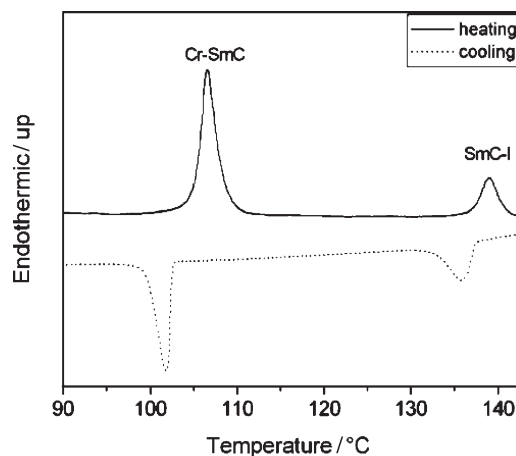

Figure 6. A representative thermogram for compounds exhibiting only SmC phases, obtained by DSC at $10°C \, min^{-1}$ showing the thermal transitions of compound **IIc**.

isotropic liquid at 139°C. The same pattern is observed on cooling.

2.3. *Fluorescence properties*

These properties were only measured for compounds 1,4-diaryl-[1,2,3]-triazoles **Ia**–**e** due to the very poor fluorescence of Schiff's base derivatives **IIa**–**c**. The UV-vis absorption and fluorescence spectroscopy data in chloroform solution for compounds **Ia**–**e** are summarized in table 2.

The UV spectra of triazoles **Ia**–**e** show an intense single band due to π–π* transitions with wavelength maxima between 274 and 297 nm ($\varepsilon = 10\,000\,mol^{-1}\,cm^{-1}$). These compounds display very weak blue emission with wavelength maxima at around 380 nm. The extension in the conjugated system and the coplanarity, as seen in compound **Ic** (with a naphthyl rigid core), lead to better results with photoluminescence quantum (Φ) yields of 22.8%, a moderate luminescence for electroluminescent device applications.

Table 2. Photophysical data of 1,4-diaryl-[1,2,3]-triazoles **Ia**–**e** in chloroform solution.

Compound	λ_{abs}/nm	λ_{em}/nm[a]	$\Phi_{Fluor.}$[b]
Ia	265	380	0.004
Ib	297	386	0.074
Ic	294	386	0.228
Id	287	385	0.092
Ie	274	380	0.005

[a]Excitation wavelength: 290 nm. [b]Determined relative to standard quinine sulphate ($\Phi_{Fluor} = 0.546$).

3. Conclusions

In summary, two series of new [1,2,3]-triazole-based liquid crystalline compounds were synthesized by applying Cu(I)-catalysed 1,3-dipolar cycloaddition of 1-azido-4-decyloxybenzene **2** to several terminal acetylenes (click-reaction). For series **Ia**–**e**, this synthetic route yielded luminescent non-linear mesogens exhibiting mainly the SmC phase within a wide temperature range, as observed by optical microscopy and DSC. Luminescence properties of this series were evaluated, showing weak blue emission peaking at around 380 nm. A second series (**IIa**–**c**) comprising three non-linear compounds containing Schiff's base units, was prepared by functional group transformation leading to an aldehyde group in the part containing the [1,2,3]-triazole, and subsequent reaction with the respective arylamines. These compounds only exhibited the SmC phase, as observed by optical microscopy and DSC, and had lower melting points compared with series **I**. All

compounds in the two series showed a stable SmC phase and are good candidates for the design of new ferroelectric materials.

4. Experimental

4.1. *Characterization*

Elemental analyses were carried out using a Perkin Elmer model 2400 instrument. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer in KBr discs. ^{1}H NMR spectra were obtained with a Varian Mercury Plus 400 MHz instrument using tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were recorded on a Varian Mercury Plus 100 MHz spectrometer. The melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 heating stage and an exposure control unit PM-30. DSC measurements were carried out using Shimadzu equipment with a DSC-50 module. A Hitachi UV-Vis model 3000 spectrophotometer was used to record absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500.

4.2. *Materials*

All the reagents were obtained from commercial sources and used without further purification. We have recently reported the synthetic procedure for 1,4-diaryl derivative compounds **Ia**–**e** [13]. The organic solvents were commercial grade except THF (HPLC grade) and all were dried by traditional methods. In general, all the compounds were purified by column chromatography on silica gel (60–120 mesh), and crystallization from analytical grade solvents. The purity of the sample was confirmed by thin layer chromatography (Merck Kieselgel 60F254).

4.3. *Synthesis*

4.3.1. [1-(4-Decyloxyphenyl)-1*H*-[1,2,3]-triazol-4-yl]methanol, 3. A mixture of 1-azido-4-decyloxybenzene **2** (2.0 g, 7.26 mmol), propargyl alcohol (0.41 g, 7.26 mmol), CuI (0.138 g, 0.726 mmol) and a catalytic amount of TEA in 30 ml of ethanol/water 1/1 mixture was stirred at 70°C for 48 h. After cooling to room temperature, the reaction mixture was filtered, washing with water, and the solid obtained was recrystallized from hexane to give a light green powder. Yield 1.9 g (79%), m.p. 85.6°C. IR (KBr) ν_{max}/cm^{-1}: 3313, 3071, 2919, 2850, 1522, 1255, 837. ^{1}H NMR (CDCl$_3$) δ: 7.89 (s, 1H), 7.59 (d, $J = 8.8$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 4.92 (s, 2H), 4.00 (t, $J = 6.4$ Hz, 2H), 2.37 (s, 1H), 1.79 (m, 2H), 1.32 (m, 14H), 0.88 (m, 3H).

4.3.2. 1-(4-Decyloxyphenyl)-1*H*-[1,2,3]-triazole-4-car-baldehyde, 4. Compound **3** (1.5 g, 4.55 mmol) dissolved in CH$_2$Cl$_2$ (5 ml) was added slowly to a suspension of MnO$_2$ (1.18 g, 13.65 mmol) in 20 ml of CH$_2$Cl$_2$ under argon. The mixture was stirred under reflux for 26 h. After cooling, the solvent was evaporated and the residue purified by column chromatography (silica gel, ethyl acetate/hexane 1/2) yielding a white solid (1.26 g, 85%), m.p. 94.6°C. IR (KBr) v_{max}/cm^{-1}: 3131, 1690, 1518, 1254, 834, 526. ^{1}H NMR (CDCl$_3$) δ: 10.21 (s, 1H), 8.43 (s, 1H), 7.64 (d, *J*=8.8 Hz, 2H), 7.04 (d, *J*=8.8 Hz, 2H), 4.02 (t, *J*=6.4 Hz, 2H), 1.82 (m, 2H), 1.28 (m, 14H), 0.88 (m, 3H).

4.3.3. (4-Decyloxyphenyl)-[1-(4-decyloxyphenyl)-1*H*-[1,2,3]-triazol-4-yl-methylene]amine, IIa. Compound **4** (0.65 g, 2.0 mmol) and *p*-decyloxyaniline (0.5 g, 2.0 mmol) in 50 ml of ethanol were heated under reflux for 12 h. The resulting solution was cooled to room temperature affording a white precipitate that was filtered and recrystallized from ethanol to give a white powder (1.06 g, 94%). IR (KBr) v_{max}/cm^{-1}: 3112, 2919, 2851, 1633, 1520, 1250, 834. ^{1}H NMR (CDCl$_3$) δ: 8.74 (s, 2H), 8.48 (s, 1H), 7.67 (d, *J*=8.8 Hz, 2H), 7.26 (d, *J*=8.4 Hz, 2H), 7.03 (d, *J*=8.4 Hz, 2H), 6.93 (d, *J*=8.8 Hz, 2H), 3.96 (m, 4H), 1.79 (m, 4H), 1.28 (m, 28H), 0.89 (t, 6H). ^{13}C NMR (CDCl$_3$) δ: 159.76, 158.39, 149.57, 147.56, 143.76, 129.90, 122.25, 122.16, 120.65, 115.42, 115.09, 68.52, 68.31, 31.91, 29.58, 29.38, 29.33, 26.06, 26.01, 22.69, 14.12. Elemental analysis for C$_{35}$H$_{52}$N$_4$O$_2$: calcd C 74.96, H 9.35, N 9.99; found C 74.58, H 9.13, N 9.33%.

4.3.4. N,N'-Bis-[1-(4-decyloxyphenyl)-1*H*-[1,2,3]-triazol-4-yl-methylene]benzene-1,4-diamine, IIb. A mixture of *p*-phenylenediamine (0.04 g, 0.343 mmol), compound **4** (0.225 g, 0.686 mmol) and molecular sieves in 30 ml of ethanol was heated under reflux for 48 h. After cooling, the precipitate was filtered and purified by recrystallization from a hexane/ethyl acetate 10/1 mixture. Yield 0.159 g (63%) of a light brown solid. IR (KBr) v_{max}/cm^{-1}: 3112, 2921, 2851, 1627, 1517, 1248, 830. ^{1}H NMR (CDCl$_3$) δ: 8.79 (s, 2H), 8.52 (s, 2H), 7.69 (d, *J*=8.0 Hz, 4H), 7.33 (s, 4H), 7.05 (d, *J*=8.0 Hz, 4H), 4.02 (t, 4H), 1.82 (m, 4H), 1.28 (m, 28H), 0.89 (t, 6H). ^{13}C NMR (CDCl$_3$) δ: 160.08, 151.77, 149.84, 147.53, 130.05, 122.46, 122.25, 121.32, 115.69, 115.32, 68.78, 32.13, 29.79, 29.60, 29.56, 29.38, 26.23, 22.92, 14.36. Elemental analysis for C$_{44}$H$_{58}$N$_8$O$_2$: calcd C 72.30, H 8.00, N 15.33; found C 71.89, H 8.15, N 15.58%.

4.3.5. N,N'-Bis-[1-(4-decyloxyphenyl)-1*H*-[1,2,3]triazol-4-yl-methylene]benzene-1,3-diamine, IIc. Compound **4**

(0.55 g, 1.67 mmol), sodium acetate (0.1 g, 1.124 mmol) and molecular sieves were added to a suspension of *m*-phenylenediamine dihydrochloride in 30 ml of ethanol. The resulting mixture was heated under reflux for 48 h, cooled to room temperature and filtered to give a solid that was purified by recrystallization from acetonitrile. Yield 0.35 g (83%) of a light yellow powder. IR (KBr) v_{max}/cm^{-1}: 3130, 2920, 2851, 1691, 1518, 1254, 833. ^{1}H NMR (CDCl$_3$) δ: 8.75 (s, 2H), 8.48 (s, 2H), 7.67 (d, *J*=9.4 Hz, 4H), 7.27 (m, 2H), 7.03 (d, *J*=9.6 Hz, 4H), 6.95 (d, *J*=9.6 Hz, 4H), 4.01 (m, 4H), 1.80 (m, 4H), 1.28 (m, 28H), 0.89 (m, 6H). ^{13}C NMR (CDCl$_3$) δ: 159.79, 158.41, 149.62, 147.55, 143.75, 129.90, 122.46, 122.52, 122.18, 120.67, 115.43, 115.09, 68.53, 68.31, 31.91, 29.57, 29.38, 29.33, 29.16, 26.05, 26.00, 22.69, 14.12. Elemental analysis for C$_{44}$H$_{58}$N$_8$O$_2$: calcd C 72.30, H 8.00, N 15.33; found C 72.16, H 8.09, N 15.45%.

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